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NON-EQUILIBRIUM THERMODYNAMICS WITH HIGHER ORDER FLUXES: BALANCE LAWS AND EXPLOITATION OF THE ENTROPY INEQUALITY

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ABSTRACT. Weakly non-local extended thermodynamics of rigid heat conductors is presented. The two celebrated procedures by Coleman-Noll and Liu for the exploitation of second law of thermodynamics are compared. It is proved that the two procedures are equivalent, if in the Coleman-Noll procedure all relevant equations are taken into account as constraints.

1. Introduction

The Navier-Stokes and Fourier theories of viscous, heat-conducting fluids provide parabolic equations and this predicts infinite pulse speeds. The attempts to find a remedy have provided an additional systematic type of thermodynamics: the extended thermodynamics [1, 2]. That theory leads to hyperbolic field equations, and thus it provides finite pulse speeds. Extended thermodynamics is a hierarchy of theories with an increasing number of fields. It is supposed that the system of governing equations is given by an arbitrary number of balance laws in which the flux at step n becomes the wanted field at step $n + 1$. The choice of the equations number depends to the accuracy of the approximation. In order to obtain a closed system of differential equations, it is necessary to choose the constitutive equations for all terms of production and for the last flux, since they cannot be obtained by any equation of the next step. The constitutive quantities will depend on all the wanted fields. This type of system stems from statistical mechanics [3]; in fact, a fundamental hypothesis of extended thermodynamics is to make the results compatible with those of the microscopic theories [1, 2]. The second law of thermodynamics restricts the constitutive equations [4] giving a deeper insight into the mathematical structure of the theory. The most celebrated techniques for the exploitation of the second law are that of Coleman-Noll [5, 6] and Liu [7, 8]. The aim of this paper is to compare the two techniques by considering the example of weakly non-local extended thermodynamics of rigid heat conductors and to prove that both the procedures are equivalent, if all relevant balances are taken into account as constraints in the Coleman-Noll technique. In Section 2 we give some more details about the 4-field theory of extended thermodynamics [2], and in Section 3 we present in a rather general form the Coleman-Noll and the Liu procedures for the exploitation of the second law. In Section 4 we investigate the conditions for which the two procedures are equivalent for weakly non-local extended thermodynamics of rigid heat conductors. Finally, the discussion of the obtained results will close the paper.

2. The 4-field theory of extended thermodynamics

In the framework of extended thermodynamics one can find two different approaches [9]: the extended irreversible thermodynamics proposed by Jou, Casas-Vázquez and Lebon [1], and the rational extended thermodynamics as developed by Müller and Ruggeri [2].

The first one postulates a system of balance laws for the evolution of dissipative fluxes, without any additional requirement. In particular the state space is larger than the set of the wanted fields, and so it is also compatible with weakly non-local theories, that are those including gradients of the wanted fields. In contrast, rational extended thermodynamics assumes that the state space is rigorously local, that means, it does not include any derivatives. Let us consider a three dimensional rigid heat conductor, and let us assume that the time rates of the specific internal energy ε and of the heat flux density \mathbf{q} satisfy the 4 following balance equations [2]

$$(1) \quad \partial_t \varepsilon + q_{i,i} = r,$$

$$(2) \quad \partial_t q_i + N_{ij,j} = -\frac{1}{\tau_R} q_i.$$

Because of the rigidity of the considered heat conductor the substantial time derivative coincides with the ordinary partial time derivative, namely we have $\frac{d}{dt} \equiv \partial_t$. The abbreviation $f_{,k} := \frac{\partial f}{\partial x_k}$, $k = 1, 2, 3$, and Einstein's convention of summation over repeated indices are used. Here r is the density of heat supply, \mathbf{N} is the flux of \mathbf{q} , and τ_R is a relaxation time whose meaning will be specified below. The name 4-field theory stems from the fact that in a 3D body first order fluxes have three components, so together with the scalar balance quantity we have four wanted quantities. It is proved in [10] that the system above can be derived in the framework of the classical non-equilibrium thermodynamics with local state space. In a solid crystal at low temperature, heat transport is due to the motion of the phonons [11]. These are quasi-particles obeying Bose-Einstein statistics. Phonons may interact with each other and with the lattice imperfections through two different types of processes:

- Normal(N)-processes, conserving the phonon momentum;
- Resistive(R)-processes in which the phonon momentum is not conserved.

The frequencies ν_N and ν_R belonging to the normal and resistive processes determine characteristic relaxation times $\tau_N = \frac{1}{\nu_N}$ and $\tau_R = \frac{1}{\nu_R}$ [12]. By choosing a suitable constitutive equation for \mathbf{N} , it is possible to recover the linearized Maxwell-Cattaneo equation from the balance of the heat flux \mathbf{q} [13]. Additionally, if we suppose that the relaxation time τ_R and the heat conductivity k are constant, then the following constitutive equation

$$(3) \quad N_{ij} = \frac{k}{\tau_R} \vartheta \delta_{ij},$$

with ϑ as absolute temperature, results in the linearized Maxwell-Cattaneo equation

$$(4) \quad \partial_t q_i + \frac{k}{\tau_R} \vartheta_{,i} = -\frac{1}{\tau_R} q_i,$$

which describes thermal wave propagation at low temperature [14, 15]. If $\tau_R \doteq 0$, we obtain the Fourier law of heat conduction

$$(5) \quad q_i = -k\vartheta_{,i}.$$

Instead, non-Fourier diffusive regime is described by the Guyer-Krumhansl equation [16, 17, 18]

$$(6) \quad \tau_R \partial_t q_i + q_i = -k\vartheta_{,i} + l_1^2 (q_{i,ll} + 2q_{l,li}).$$

Here l_1 has the dimension of a length and depends on τ_N . Let us notice that (6) can be obtained also in the framework of classical irreversible thermodynamics with first order non-local state space [19]. In the linear case an admissible expression for N_{ij} is [20]

$$(7) \quad N_{ij} = \frac{k}{\tau_R} \vartheta \delta_{ij} - L_1 q_{i,j} - L_2 q_{j,i} - L_3 q_{k,k} \delta_{ij}.$$

Here L_1 , L_2 and L_3 are constants. The Guyer-Krumhansl equation is recovered by (2) and (7) under the additional assumption

$$(8) \quad L_1 = L_2 = L_3 = -\frac{l_1^2}{\tau_R}.$$

The considerations above suggest that the complete description of heat propagation, which encompasses all the well known theories, requires a gradient generalization to the extended thermodynamic approach. This fact motivates our investigation of Coleman-Noll and Liu procedures in this case.

3. Coleman-Noll and Liu procedures

The aforementioned constitutive equations of heat conduction are restricted by the second law of thermodynamics, and so it seems to be important to analyze and compare the different techniques of its exploitation.

General formulation:

Let us indicate by $u_n(t, x_\nu)$, $n = 1 \dots N$, $\nu = 1, 2, 3$ the wanted thermodynamical fields, [21, 22, 23]. The change in time of these basic fields is governed by the following first order hierarchical system of balance laws

$$(9) \quad \partial_t u_n + F_{\mu,\mu}^n = \sigma_n,$$

where \mathbf{F}^n and σ_n are the flux and the production of the field u_n , respectively. To close the system (9), one needs constitutive equations for the N -th flux \mathbf{F}^N and for the N productions σ_n , $n = 1, 2 \dots N$. First order weakly non-local thermodynamics [1] postulates these equations in the form

$$(10) \quad \mathbf{F}^N = \mathbf{F}^N(u_n, u_{n,\nu}), \quad \sigma_n = \sigma_n(u_n, u_{n,\nu}).$$

Here \mathbf{F}^N and σ_n are suitable real functions which cannot be chosen arbitrarily, because they have to satisfy the second law. Let us assume that these equations are independent, in the sense that none of them can be obtained from the other ones by a linear combination. Inserting the constitutive equations (10) into the balances (9) results in the the system of

differential equations which has to be solved finally [21]. For exploiting the second law, we need the local balance of entropy, which takes the form

$$(11) \quad \partial_t S + F_{\mu,\mu}^S - \sigma_S \geq 0,$$

where S is the entropy density, \mathbf{F}^S is the entropy flux and σ_S the density of entropy supply. In order to calculate the left hand side (11), namely the total rate of entropy production per unit of volume, we have to consider the constitutive equations of the entropy density and of the entropy flux, which are not included into the set (10). The principle of equipresence imposes that S and \mathbf{F}^S depend on the same variables as the other constitutive functions do. Then we assume

$$(12) \quad S = S(u_n, u_{n,\nu}), \quad \mathbf{F}^S = \mathbf{F}^S(u_n, u_{n,\nu}).$$

Because of (11) and (12), we get the dissipation inequality, which can be expressed in the general form

$$(13) \quad I(u_n, \partial_t u_n, u_{n,\nu}, \partial_t u_{n,\nu}, u_{n,\nu\mu}) \geq 0.$$

The entropy principle requires that any solution of the balance equations for given initial conditions and inserted constitutive equations has to satisfy the dissipation inequality (13). This principle is the formulation of the second law by Coleman-Mizel [24]. The entropy principle can be exploited in by different procedures, according to the technique which is used in order to take into account the balance laws. The exploitation procedure becomes easier, if the system of field equations is linear in the highest derivatives of the wanted fields in the state space. Since this is the usual context, it is possible to proceed with the construction of a method to satisfy the dissipation inequality (13).

Coleman-Noll method:

Here, we consider that version of the Coleman-Noll technique in which the inequality (13) is transformed by substituting all the balance laws into the local entropy inequality, regarding them as constraints [5, 6]. If not all balances were introduced into (13), the class of materials becomes smaller than necessary, but the second law is satisfied for this restricted class of materials.

Liu method:

In the Liu technique the inequality (13) is transformed by coupling the local entropy inequality with a linear combination of the field equations. The factors in this linear combination of the balance equations are called Lagrange multipliers [7, 8].

In both the cases, the thermodynamic restrictions on the constitutive functions stem from the linearity of the obtained inequality with respect to the higher derivatives of the wanted fields which are considered to be totally arbitrary. In a recent paper [25] is proved that for rigid bodies with internal variables the two methods of exploiting the second law are equivalent, if all balances are taken into account, that means, both methods result in the same thermodynamic restrictions for the constitutive equations. Here we prove their equivalence in the 4-field theory of weakly non-local extended irreversible thermodynamics.

4. Equivalence of the procedures

Assuming that the evolution of the temperature and of the heat flux is governed by the 4-field system (1) and (2), the entropy principle requires that

$$(14) \quad \partial_t s + J_{l,l} - \sigma_s \geq 0.$$

the chosen state space is

$$(15) \quad Z = \{\varepsilon, q_i, \varepsilon_{,i}, q_{i,j}\},$$

Thus, the inequality (14) on the state space takes the form

$$(16) \quad \begin{aligned} & \frac{\partial s}{\partial \varepsilon} \partial_t \varepsilon + \frac{\partial s}{\partial q_i} \partial_t q_i + \frac{\partial s}{\partial \varepsilon_{,i}} \partial_t \varepsilon_{,i} + \frac{\partial s}{\partial q_{i,j}} \partial_t q_{i,j} + \\ & + \frac{\partial J_i}{\partial \varepsilon} \varepsilon_{,i} + \frac{\partial J_i}{\partial q_j} q_{j,i} + \frac{\partial J_i}{\partial \varepsilon_{,j}} \varepsilon_{,ji} + \frac{\partial J_i}{\partial q_{j,k}} q_{j,ki} - \sigma_s \geq 0. \end{aligned}$$

According to the Coleman-Noll procedure, let us substitute the time derivatives of ε and q_i by the system of balance laws. Then, due to the thermodynamic relation

$$(17) \quad \frac{\partial s}{\partial \varepsilon} = \frac{1}{\vartheta},$$

and under the additional assumption

$$(18) \quad \sigma_s = \frac{r}{\vartheta},$$

we obtain the Coleman-Noll inequality

$$(19) \quad \begin{aligned} & \frac{\partial s}{\partial \varepsilon_{,k}} \partial_t \varepsilon_{,k} + \frac{\partial s}{\partial q_{i,k}} \partial_t q_{i,k} - \frac{1}{\tau_R} \frac{\partial s}{\partial q_i} q_i + \left(-\frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial \varepsilon} + \frac{\partial J_l}{\partial \varepsilon} \right) \varepsilon_{,l} + \\ & + \left(-\frac{\partial s}{\partial \varepsilon_{,k}} - \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial q_k} + \frac{\partial J_l}{\partial q_k} \right) q_{k,l} + \left(\frac{\partial J_l}{\partial \varepsilon_{,k}} - \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial \varepsilon_{,k}} \right) \varepsilon_{,kl} + \\ & + \left(\frac{\partial J_l}{\partial q_{k,j}} - \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial q_{k,j}} \right) q_{k,jl} \geq 0. \end{aligned}$$

Because the higher derivatives can be chosen arbitrarily, and because the factors before the higher derivatives are independent of them, they have to be zero, since otherwise the dissipation inequality (19) can be destroyed by choosing the higher derivatives. Thus, we obtain the thermodynamic restrictions

$$(20) \quad \frac{\partial s}{\partial \varepsilon_{,k}} = 0,$$

$$(21) \quad \frac{\partial s}{\partial q_{i,k}} = 0,$$

$$(22) \quad \frac{\partial J_l}{\partial \varepsilon_{,k}} = \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial \varepsilon_{,k}},$$

$$(23) \quad \frac{\partial J_l}{\partial q_{k,j}} = \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial q_{k,j}},$$

$$(24) \quad -\frac{1}{\tau_R} \frac{\partial s}{\partial q_i} q_i + \left(-\frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial \varepsilon} + \frac{\partial J_l}{\partial \varepsilon} \right) \varepsilon_{,l} + \\ + \left(-\frac{\partial s}{\partial \varepsilon} \delta_{kl} - \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial q_k} + \frac{\partial J_l}{\partial q_k} \right) q_{k,l} \geq 0.$$

We now consider the entropy inequality (16) again and introduce the two Lagrange multipliers λ and $\Lambda_i, i = 1, 2, 3$. Then, the Liu inequality is given by

$$(25) \quad \left(\frac{\partial s}{\partial \varepsilon} - \lambda \right) \partial_t \varepsilon + \left(\frac{\partial s}{\partial q_i} - \Lambda_i \right) \partial_t q_i + \frac{\partial s}{\partial \varepsilon_{,k}} \partial_t \varepsilon_{,k} + \frac{\partial s}{\partial q_{i,k}} \partial_t q_{i,k} + \\ + \left(\frac{\partial J_l}{\partial \varepsilon} - \Lambda_i \frac{\partial N_{il}}{\partial \varepsilon} \right) \varepsilon_{,l} + \left(\frac{\partial J_l}{\partial q_k} - \Lambda_i \frac{\partial N_{il}}{\partial q_k} - \lambda \delta_{kl} \right) q_{k,l} + \\ + \left(\frac{\partial J_l}{\partial \varepsilon_{,k}} - \Lambda_i \frac{\partial N_{il}}{\partial \varepsilon_{,k}} \right) \varepsilon_{,kl} + \left(\frac{\partial J_l}{\partial q_{k,j}} - \Lambda_i \frac{\partial N_{il}}{\partial q_{k,j}} \right) q_{k,jl} + \\ - \sigma_s + \lambda r - \frac{1}{\tau_R} \Lambda_i q_i \geq 0.$$

Using the same argumentation as before, we obtain the following restrictions

$$(26) \quad \lambda = \frac{\partial s}{\partial \varepsilon},$$

$$(27) \quad \Lambda_i = \frac{\partial s}{\partial q_i},$$

$$(28) \quad \frac{\partial s}{\partial \varepsilon_{,k}} = 0,$$

$$(29) \quad \frac{\partial s}{\partial q_{i,k}} = 0,$$

$$(30) \quad \frac{\partial J_l}{\partial \varepsilon_{,k}} = \Lambda_i \frac{\partial N_{il}}{\partial \varepsilon_{,k}},$$

$$(31) \quad \frac{\partial J_l}{\partial q_{k,j}} = \Lambda_i \frac{\partial N_{il}}{\partial q_{k,j}},$$

$$(32) \quad -\frac{1}{\tau_R} \Lambda_i q_i + \left(-\Lambda_i \frac{\partial N_{il}}{\partial \varepsilon} + \frac{\partial J_l}{\partial \varepsilon} \right) \varepsilon_{,l} + \\ + \left(-\lambda \delta_{kl} - \Lambda_i \frac{\partial N_{il}}{\partial q_k} + \frac{\partial J_l}{\partial q_k} \right) q_{k,l} - \sigma_s + \lambda r \geq 0.$$

Substituting the expressions of the Lagrange multipliers λ and Λ_i , obtained by the first two restrictions above and taking into account (18), we recover the relations (20)-(24).

Consequently, the equivalence of Coleman-Noll and Liu procedures is proved, since the obtained thermodynamic restrictions and the reduced dissipation inequality are the same.

We now consider the constitutive state space

$$(33) \quad Z = \{\varepsilon, q_i\}.$$

The thermodynamic restrictions obtained by both the procedures are

$$(34) \quad \frac{\partial J_l}{\partial \varepsilon} = \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial \varepsilon},$$

$$(35) \quad \frac{\partial J_l}{\partial q_k} = \frac{\partial s}{\partial \varepsilon} \delta_{kl} - \frac{\partial s}{\partial q_i} \frac{\partial N_{il}}{\partial q_k},$$

$$(36) \quad -\frac{1}{\tau_R} \frac{\partial s}{\partial q_i} q_i \geq 0.$$

If we make the additional assumption outside the usual exploitation scheme that the entropy density may not depend on the heat flux density, then the second thermodynamic restriction above yields

$$(37) \quad J_l = \frac{q_l}{\vartheta},$$

which is the classical form of the entropy flux often postulated in rational thermodynamics [6].

It is worth noticing that the form of the entropy flux is one of the main differences between Coleman-Noll and Liu approaches. In fact Coleman and Noll assume that the entropy flux takes the form (37) [5], while Liu regards the entropy flux as a general constitutive function. In this sense the Liu method seems to be designed for a more general class of materials. It is proved in [26] that, if this difference is maintained, then the two methods lead to different results. However, here we have removed the Coleman-Noll hypothesis on the entropy flux, proving that their technique for the exploitation of second law still works. Moreover, the results we obtained in this case are the same obtained by the application of the Liu method.

Another property which also deserves consideration follows by the reduced dissipation inequality (36). In fact, in classical irreversible extended thermodynamics it is usual to consider the specific entropy in the form [27]

$$(38) \quad s = s_0(\varepsilon) + \frac{1}{2} m_{ij}(\varepsilon, q^2) q_i q_j.$$

The assumption that m_{ij} is negative definite ensures that the principle of the maximum entropy at equilibrium is fulfilled [1, 27].

However, if m_{ij} does not depend on q^2 , by substituting (38) into the inequality (36), it is easily to be seen that the negative definiteness of m_{ij} is a consequence of the second law of thermodynamics.

5. Conclusions

The equivalence of Coleman-Noll and Liu techniques for the exploitation of the second law has been proved in the framework of weakly non-local extended thermodynamics. We have considered the 4-field gradient theory of rigid heat conductors, and we have shown that both procedures results in the same thermodynamic restrictions.

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